SURFACE STRUCTURES AND TRANSITIONS AND THE EVOLUTION FROM FIRM TO BULK BEHAVIOR

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Final Report

Surface Structure and Transitions and the Evaluation

from Film to Bulk Behavior

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This research program has concentrated on two main areas of research: (a) the structures and transitions of monolayers and multilayers of rare gases including krypton and xenon on single crystal graphite (b) the thermal roughening of simple metal surfaces. We summarize below our principal results on these two problems.

As is now well known, the simple systems of rare gases on a triangular surface have shown a remarkable variety of solid phases. This is due to the substrate potential which may have a slightly different periodicity from the bulk phase of the adsorbed species. Until this work, high resolution x-ray scattering experiments were confined to powder substrates such as ZYX and vermicular graphite. Advances in cell powder design, together with high brightness synchrotron radiation x-ray sources, have made possible studies on one single crystal substrate; this allows one to investigate the structures and orientations of these solid layers in fine detail. Although electron diffraction techniques have been used for monolayers on single crystal graphite, their diagnostic power is severely limited by low resolution and multiple scattering.

We have investigated Xe monolayers on a single crystal graphite surface using beam-line X-20A at NSLS. We used a 1 mm x 1 mm focused beam with an Si double monochromator and a Ge analyzer. In the sample cell we used vermicular graphite powder as a ballast to control the surface coverage. Kr monolayers have also been investigated

with the same apparatus. A few torr of He gas was added to the cell below 80 K in order to ensure thermal equilibrium and uniformity through the sample cell. The experiment surveyed the coverage (f) range from .87 to 1.00 monolayers. For each coverage, data were taken from just below the melting temperature T_m, (for f = .88, T_m = 125 K) down to about 20 K in steps of ~ 5 degrees K. We take the point B_1 in the krypton isotherm as the definition of f = 1 monolayer.

Above 75 K ,the Xe monolayer exhibits the same behavior at all coverages. Just below T_m the monolayer has an incommensurate (IC) solid structure with the axes aligned with those of the substrate. As the temperature is lowered, the wave vector Q of the Xe (1,0) Bragg peak increases continuously. At Q ~ 1.625 $Å^{-1}$ and at about 15 °K below T_m, the Xe monolayer starts to rotate with respect to the graphite substrate. This rotated Xe phase was predicted theoretically and previously observed experimentally, but has not been studied carefully. The rotation angle seems to jump from zero to a value of ~ .5°. Initially only a small fraction of the layer rotates while the major portion stays aligned. After changing the temperature, it takes a few hours for the rotated monolayer to come to equilibrium. As the sample is cooled further, Q increases up to 1.675 $Å^{-1}$ (at T = 26.8 K), which is smaller than Q_c, the $\sqrt{3}$ x $\sqrt{3}$ commensurate value, 1.70 $Å^{-1}$. The monolayer also stays rotated although α continues to decrease. For the coverages of .93 and 1.0, the monolayer realigns with respect to the substrate. This realignment occurs at T ~ 65 °K for f = .93 and T ~ 70 °K for f = 1.0. Whenever the monolayer realigns of α becomes small (< .1°), we see pronounced hexagonal domain wall modulation peaks. The realigned phases only exist over about 10 °K in temperature before they undergo a C-IC transition. The monolayer has C-IC transition at T ~ 54 °K for f = .93 and T ~ 66 °K for f = 1.0. At the transition, a C phase coexists with an IC phase (Q_{ic} ~ 1.69 $Å^{-1}$) and the C phase peak continues to grow at the expense of the IC phase for several hours; however, the IC peak never disappears completely. On cooling, the C phase peak sharpens but the limiting radial

width is considerably broader than that for the Kr C phase peak. Further, considerable scattering still exists for Q less than Q_c. We have not yet observed on the single crystal substrate the superlight wall stripe phase which was reported earlier and predicted theoretically as discussed below. The earlier observation of the stripe phase may be due to finite size effects.

On the theoretical side, light and superlight wall energies for a xenon monolayer on graphite were calculated by a classical zero-temperature relaxation scheme. Phase diagrams were then obtained using a striped helical Potts model for domain wall networks (such as striped or hexagonal incommensurate solids). The commensurate-incommensurate transition noted in past electron diffraction experiments was reinterpreted as a structural transition between two incommensurate solids, in agreement with the recent x-ray scattering work mentioned above. Matching experimental transition lines led to estimates for various interatomic potentials. We also studied the pre-emption of the incipient commensurate phase by condensation of the bilayer.

We have also carried out high resolution x-ray diffraction studies of the structures and phase transitions of monolayer krypton, adsorbed on both powder and single crystal graphite substrates. A comprehensive series of powder diffraction profiles is used to construct the two dimensional phase diagram. The melting of the $\sqrt{3}$ x $\sqrt{3}$ commensurate solid is shown to be strongly first order throughout the region where tricritical behavior was previously thought to occur; fluid solid coexistence extends up to the termination of the commensurate phase at 130 K. A disordered weakly incommensurate phase is shown to be a reentrant fluid, a system which may be described as a disordered network of domain walls and which evolves continuously into a more conventional 2D fluid. This evolution is marked by the disappearance of satellite peaks which are caused by the modulation of the overlayer by the substrate. The freezing of the reentrant fluid into the commensurate phase

is shown to be consistent with a chiral Potts transition, its freezing into the incommensurate solid consistent with a dislocation binding transition.

Single crystal experiments reveal the orientation of the weakly incommensurate phase. The reentrant fluid is found to have no visible orientational fluctuations, manifesting isotropic diffraction peaks. This is attributed to the strong epitaxy of domain walls. The incommensurate solid is shown to undergo an aligned-rotated transition which is well described by zero-temperature calculations.

As a natural extension of our x-ray scattering studies of monolayers on single crystal graphite, multilayers of rare gases on single crystal graphite have been studied. Among physisorbed gases on graphite, xenon and krypton are believed to wet completely to form a solid film on graphite. For scattering intensity considerations, we chose the xenon/graphite system over that of krypton/graphite. We have been able to observe directly the growth of the adsorbed layers. The detailed structures and orientation of the layers have been observed as the layers evolve into a thick film. We studied carefully the out-of-plane scattering from the layers, as well as in the in-plane scattering, which was a major concern of the monolayer study. From the out-of-plane scattering, it was possible to deduce the number of layers in the film and the stacking order. Contrary to naive expectations, the thin layers of xenon do not grow with so called "ABC" stacking order. Even the simplest system of complete wetting must be scrutinized further.

Finally, we have begun systematic studies of the spontaneous thermal roughening of simple metal surfaces. It has been predicted for some time that for simple surfaces an instability could occur in which the amplitude of thermally excited capillary waves becomes sufficiently large that the surface roughness diverges logarithmically with the size of the system. On an atomic level, this transition results from the proliferation of atomic steps and islands on the crystalline surface. The concept of a roughening transition has played a

central role in theories of crystal growth and equilibrium crystal shapes and has been used empirically by experimentalists for many years. Nonetheless, the nature of this transition and indeed its very existence remains controversial.

X-rays might not initially seem to be an ideal probe of interface roughening. However, x-rays may be made surface sensitive by using a glancing angle geometry and by studying a surface Bragg peak which is bulk-forbidden. Scattering from bulk-forbidden peaks turns out to reflect directly the structure of the surface. Specifically, by a detailed analysis of the lineshape one can extract information about the geometrical distribution of steps on the surface. For a smooth surface the Bragg peak lineshape is a Gaussian modified by surface finite-size effects and instrumental resolution. For a rough surface the line shape is a power law singularity $(Q - Q_{Bragg})^{-2+\eta}$.

We have studied the scattering from the (110) surface Bragg peak of the Silver (110) surface. We find that as a function of increasing temperature this surface Bragg peak evolves considerably in shape and intensity, developing very large tails at high temperatures. A detailed line-shape analysis, with minimal assumptions, reveals that the true Bragg scattering vanishes at 450 ± 25 °C and that above this temperature the surface peak is well-described as a power law singularity. Above about 600 °C the surface peak is barely observable so that, heuristically, the surface no longer exists - presumably due to the proliferation of steps and islands.

We have thus provided direct, model-independent evidence for a transition between smooth and logarithmically rough phases of a clean metal surface. Further, we have demonstrated that glancing angle x-ray scattering can provide direct information about thermal variations of the surface height-height correlation function. Below the transition, the scattering is a combination of Bragg scattering and tails, with the Bragg intensity dropping to zero at T_R. Above T_R, the data are described by a power law lineshape with η

increasing rapidly through $\simeq 0.6$ near the transition. Given the relative simplicity of Ag (110), we hope that these results will stimulate calculations of surface roughening based on specific, realistic potentials.

On the theoretical side, we have studied the effects of imperfections on roughening and facet formation. Imperfections can originate from either impurity particles, or screw dislocations terminating on the surface. Roughening proceeds by formation of steps on the crystal surface. The meandering of these steps is severely modified by pinning to impurities. These effects can be probed directly by scanning microscopy, or indirectly by examining facet formation. The role of impurities on the roughening transition is being addressed, for the first time, in our studies.

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